Reaction of Azoalkanes with Isolable Cation Radical Salts

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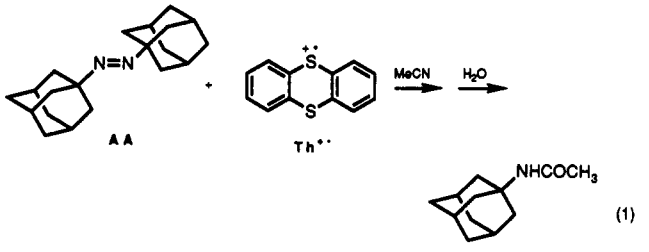
Three tertiary azoalkanes related in the sense acyclic, cyclic, and bicyclic are shown to evolve nitrogen upon oxidation with stable cation radical salts. Thus azo-*tert*-octane (ATO), 3,3,6,6-tetramethyl-1,2-diazacyclohexene (TMDAC), and 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (Me_2DBO) react rapidly with thianthrenium perchlorate ($Th^{\bullet+}ClO_4^-$), tris(*p*-bromophenyl)aminium hexachloroantimonate ($TBPA^{\bullet+}SbCl_6^-$), and $TBPA^{\bullet+}SbF_6^-$. The ether and olefin products, which are formed in high yield in CH_2Cl_2/MeOH solvent, are not those expected from the usual free-radical decomposition of azoalkanes but instead implicate carbocations. Although the reaction stoichiometry clearly requires 2 equiv of cation radical salt to one of azoalkane, the mechanism is not yet clearly defined. A complication in these studies is found in the ability of certain cation radical salts to oxidize more azoalkane than expected based on the 2:1 stoichiometry.

Although azoalkanes are widely used sources of radicals and biradicals,[1] we reported in 1985 that reaction of 1,1′-azoadamantane (AA) with thianthrenium perchlorate ($Th^{\bullet+}ClO_4^-$) in MeCN afforded the Ritter product, 1-adamantyl acetamide (eq 1), in a process typical of adamantyl cations.[2] Thermolysis of AA alone to yield nitrogen plus adamantyl radicals requires heating to 300 °C, yet this cation radical induced oxidation proceeded rapidly at room temperature. A survey of azoalkane reactivity in our laboratories soon demonstrated that many such compounds do not yield nitrogen on treatment with cation radical salts. In particular, 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO) gave red salts **1** and **2** but no N_2 on reaction with $Th^{\bullet+}ClO_4^-$ and with the well-known isolable cation radical salt tris (*p*-bromophenyl)aminium hexachlorantimonate ($TBPA^{\bullet+}SbCl_6^-$), respectively.[3]



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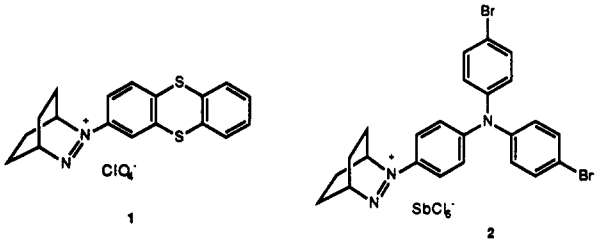
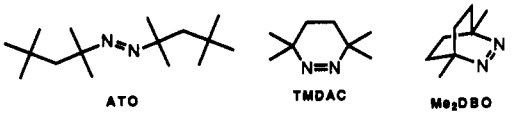


We now present a detailed account of the cation radical induced oxidation of three tertiary azoalkanes related in the sense acyclic, cyclic, and bicyclic; namely azo-*tert*-octane (ATO), 3,3,6,6-tetramethyl-1,2-diazacyclohexene (TMDAC), and 1,4-dimethyl-2,3-diazabicyclo[2.2.2]oct-2-ene (Me_2DBO). Though we looked briefly at the reactions



of azo-*tert*-butane, ATO was deemed more suitable for studying the formation of products because of their higher molecular weights and, hence, easier assay. All of these azoalkanes were oxidized rapidly and quantitatively at room temperature to give nitrogen plus cation derived products. Before discussing our current results, we first present a brief survey of prior work on the one-electron oxidation of azoalkanes.

The One-Electron Oxidation of Azoalkanes. In order to study the reaction of radicals with cation radical salts, Kim refluxed azoisobutyronitrile (AIBN) with $Th^{\bullet+}ClO_4^-$ in MeCN.[4] The color of $Th^{\bullet+}$ disappeared in 40 min using an excess of AIBN, but no product containing Th linked to either AIBN or to the 2-cyanopropyl moiety was isolated. Instead, the compounds identified in the intractable mixture included thianthrene oxide and tetramethylsuccinonitrile. Again, in seeking to examine the reaction of radicals with cation radicals, Shine et al.[5] planned to irradiate azo-*tert*-butane (ATB) with $Th^{\bullet+}ClO_4^-$ but they found that these compounds reacted rapidly in the absence of light. Although a quantitative study of the related ATO system is part of the present report, the above results already show the much greater reactivity of $Th^{\bullet+}$ with ATB than with AIBN. Kim also noted the facile reaction of an azoalkane with $Th^{\bullet+}ClO_4^-$.[6] Thus azobis(2-phenoxy-2-propane) led to phenol and 5-(4-hydroxyphenyl)thianthreniumyl perchlorate, but the yield of recovered propyl units was low and this azoalkane is too complicated to allow for mechanistic conclusions. Engel et al. found that irradiation of 1-cyclopropylDBO in CCl_4[7] or of 1-phenylDBO in $BrCCl_3$[8] gave products that implicated azoalkane cation radicals as intermediates. The collaborative effort of the present authors, which began in 1983, is an outgrowth of the discoveries made in their laboratories.[5,7]

The cerric ammonium nitrate induced deazatation of substituted 1-pyrazolines reported by Martelli and Grée[9]

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Table I. Products of Reaction of ATO with $TBPA^{\bullet+}SbX_6^-$ in 3:1 CH_2Cl_2–MeOH

reactants,[a] μmol				products, μmol (%)							product balance,[c] μmol (%)		
run no.	ATO	$TBPASbX_6$	DTBP[b]	recov ATO	N_2	4	5	6	7	8	*tert*-octyl	ATO + *tert*-octyl	ATO + N_2
1	50.6	50.7[d]	110	27	29	1.3	17	2.7	27	0.6	24	51	55
				(52)	(57)[e]	(1.3)[f]	(17)	(2.7)	(26)	(0.6)	(48)	(100)	(109)
2	62.1	62.3[d]	130	34	31	*g*	19	3.2	33	<0.1	27	61	65
				(55)	(50)		(15)	(2.6)	(26)		(44)	(99)	(105)
3	62.1	124[d]	125	0.6	60	*g*	42	5.3	82	<0.1	65	65	61
				(1.0)	(97)		(34)	(4.3)	(66)		(104)	(105)	(98)
4	45.4	92.0[h]	92.0	0.1	45	1.3	50	4.6	37	0.3	47	47	45
				(0.1)	(99)	(1.4)	(55)	(5.1)	(40)	(0.3)	(104)	(104)	(99)

[a] Solvent volume 4.0 mL in runs 1–3 and 2.0 mL in run 4. [b] 2,6-Di-*tert*-butylpyridine. [c] μmol = (sum of products containing *tert*-octyl groups)/2 because ATO contains two *tert*-octyl groups. % = total % of *tert*-octyl products 4–8. [d] $TBPASbF_6$. [e] Anomalously high N_2 yield due to failure to degas the MeOH. [f] GC peak only partially resolved from solvent impurity. [g] Solvent impurity prevented quantification. [h] $TBPASbCl_6$. Products analyzed 3 days after decolorization. 1.3 μmol of *tert*-octyl chloride also found and included in product balance.

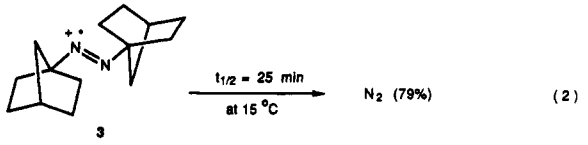
Table II. Products of Reaction of ATO with $Th^{\bullet+}ClO_4^-$ in CH_2Cl_2

reactants, μmol			products, μmol (%)[a]							product balance, μmol (%)			
run no.	ATO	$ThClO_4$	4	5	6	7	8	Th	ThO[b]	$Th^{\bullet+}$ consumed[c]	(*tert*-octyl)[d]/2	balance[e]	Th recovered[f]
1[g]	61.5	101	tr	34	5.1	63	tr	104	3.4	94	51	0.54	
				(28)	(4.2)	(51)		(103)	(3.4)		(83)	(108)	(107)
2[h]	59.7	101	3.2	75	15	6.0	tr	95	2.8	95	50	0.52	
			(2.9)	(63)	(13)	(5.0)		(94)	(2.7)		(84)	(104)	(97)
3[h]	54.2	101	2.8	73	14	5.8	tr	99	2.8	95	48	0.50	
			(2.6)	(67)	(13)	(5.4)		(99)	(2.8)		(88)	(100)	(101)
4[h]	56.7	101	2.4	78	14	7.6	tr	108	4.5	92	51	0.55	
			(2.1)	(69)	(12)	(6.7)		(107)	(4.4)		(90)	(111)	(113)

[a] Each result is the average of three GC analyses. *tert*-$BuNH_2$ was injected into the reaction mixture immediately after decolorization of $Th^{\bullet+}$ had occurred, in order to neutralize $HClO_4$. [b] Thianthrene oxide. [c] $Th^{\bullet+}$ consumed by reaction with ATO = initial $ThClO_4$ minus 2 ThO. [d] See Table I footnote c. [e] An excess (see columns 2 and 3) of ATO was used. A ≡ ATO consumed to form *tert*-octyl products = (*tert*-octyl)/2. B ≡ $Th^{\bullet+}$ consumed to form *tert*-octyl products. Balance = A/B. % balance = 2 × 100 A/B because each ATO requires $2Th^{\bullet+}$. [f] C ≡ Th expected = $Th^{\bullet+}$ consumed in reaction with ATO plus ThO found since reaction of $Th^{\bullet+}$ with H_2O produces equal amounts of Th and ThO. D ≡ Th found. Th recovered ≡ D/C. [g] 9.90 mmol of MeOH present in reaction mixture. [h] MeOH added only during workup.

predates the work with azoalkanes and stable cation radical salts. Adam and co-workers not only extended this observation to larger ring azoalkanes,[10,11] but they also found that electronically excited 2,4,6-triphenylpyrylium salts would oxidatively deazatize bicyclic and polycyclic azoalkanes.[12]

Although azoalkane cation radicals had been identified by ESR as transient species in 1988,[13-15] Mendicino and Blackstock demonstrated that the cation radical of 1,1′-azonorbornane (**3**) possessed considerable kinetic stability (eq 2).[16] Cation radical **3** was even capable of oxidizing



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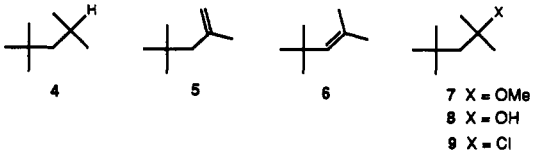
thianthrene to $Th^{\bullet+}$, an interesting reversal of the usual role of azoalkanes and cation radical salts.

Product Studies. Cation radical induced oxidation of ATO, TMDAC, and Me_2DBO leads to alkyl cations, which may exist as ion pairs or in equilibrium with complexes with weak nucleophiles. These cationic intermediates are captured by stronger nucleophiles or undergo elimination to form olefins. The oxidation products **4–8** of ATO were



4 5 6 7 X = OMe 8 X = OH 9 X = Cl

identified and quantified by capillary GC, using the method of "standard addition" of authentic samples[17] (cf. Tables I and II). In the case of $TBPA^{\bullet+}$ (Table I), unreacted ATO was also determined by GC while N_2 was measured with a Töpler pump and gas buret. Runs 1 and 2 in Table I show that at a reactant ratio (cation radical salt:azoalkane) of 1:1, half of the ATO is recovered and half goes to N_2 plus the *tert*-octyl products **4–8**. When the initial ratio of $TBPA^{\bullet+}$ to ATO was 2:1 (runs 3 and 4), all of the *tert*-octyl groups appeared as **4–8**. With the exception of **4** (1.3%), these compounds are all characteristic products of *tert*-octyl cations. GC analysis of run 2 revealed that TBPA was the only triarylamine present. Run 4 reports reaction products of ATO with $TBPA^{\bullet+}SbCl_6^-$ measured three days after the cation radical color had disappeared. Among the products listed is *tert*-octyl chloride **9** (1.3 μmol, 1.4%). It was found, in fact, that initially much more (20%) **9** had been formed but this amount decreased over the 72-h period with a corresponding rise in the amount of **5**. *tert*-Octyl chloride is attributed to reaction of *tert*-octyl cation with the $SbCl_6^-$ counter ion,[18] and elimination of HCl is surely caused by the 2,6-di-*tert*-butyl pyridine (DTBP) that was present.

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Table III. Products of Reaction of TMDAC with $Th^{\bullet+}ClO_4^-$ in $MeOH/CH_2Cl_2$

reactants,[a] μmol			products, μmol (%)					product balance, μmol (%)
run no.	TMDAC	$ThClO_4$	recov TMDAC	Th[b]	10	11	12	TMDAC + alkyl[c]
1[d]	45.3	91.2	trace	88 (96)	5.7 (13)	6.0 (13)	32 (70)	43 (96)
2[d]	52.9	104	1.6 (3.0)	100 (96)	7.3 (14)	6.0 (13)	34 (64)	52 (98)

[a] Solvent was 6.0 mL of a 9.90 mM solution of MeOH in CH_2Cl_2. [b] Thianthrene. A trace of thianthrene 5-oxide was observed in both runs. [c] Sum of alkyl products 10–12 plus recovered TMDAC. [d] $HClO_4$ was neutralized with Et_3N; see Table II, footnote a.

Table IV. Products of Reaction of Me_2DBO with $TBPASbF_6$ in 3:1 CH_2Cl_2–MeOH

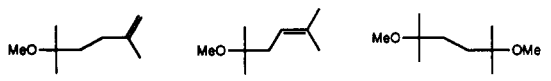
reactants, μmol				products, μmol (%)									product balance, μmol (%)		
Me_2DBO	$TBPASbF_6$	DBMP[a]	solv., mL	recov Me_2DBO	N_2	19	20	21	22	23	24t	24c	alkyl[b]	Me_2DBO + alkyl	Me_2DBO + N_2
140	140	281	4.2	74	67	0.3	0.8	1.2	1.5	31	21	8.8	65	138	140
				(53)	(48)	(0.2)	(0.6)	(0.9)	(1.1)	(22)	(15)	(6.3)	(46)	(99)	(100)
124	248	248	4.0	10	128	0.7	1.4	7.1	2.3	51	35	6.9	105	115	138
				(8.3)	(103)[c]	(0.5)	(1.1)	(5.7)	(1.8)	(41)	(29)	(5.5)	(85)	(93)	(111)
147[d]	296	302	4.3	11	131	1.1	3.5	2.4	2.5	72	43	12.6	137	148	142
				(7.2)	(89)	(0.8)	(2.4)	(1.4)	(1.7)	(49)	(29)	(8.6)	(93)	(101)	(97)

[a] 2,6-Di-*tert*-butyl-4-methylpyridine. [b] Sum of products containing the 1,4-dimethylcyclohexane group, excluding Me_2DBO. [c] Repeat experiment gave 88% N_2 yield, suggesting that the 103% is anomalously high. [d] Run at 0 °C.

When $TBPA^{\bullet+}SbF_6^-$ was used as the oxidant, the product composition remained constant with time. It was found also that use of $TBPA^{\bullet+}SbCl_6^-$ in less than 2:1 ratio of reactants led to a slow secondary oxidation of ATO and TMDAC, a phenomenon that is discussed later.

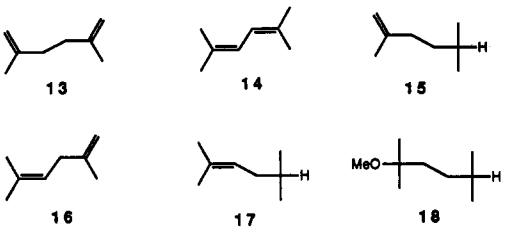
The reaction products 4–8 of ATO with $Th^{\bullet+}ClO_4^-$ are listed in Table II. In each of the four runs, an excess of ATO over $Th^{\bullet+}ClO_4^-$ was used (i.e., more ATO than is required by the ratio $Th^{\bullet+}$/ATO of 2:1). Since we measured neither the amount of unreacted ATO nor N_2 that was formed, the "balance" of products (column 13) was calculated in the following way. The $Th^{\bullet+}$ that was consumed reacted either with ATO (in excess) or with the small amount of adventitious water present in the solvent. Reaction with water led to thianthrene (Th) and thianthrene 5-oxide (ThO) according to the equation $2\ Th^{\bullet+} + H_2O \rightarrow Th + ThO + 2H^+$. The amount of ThO produced (column 10) then reveals how much $Th^{\bullet+}$ reacted with H_2O and hence how much (the remainder) must have reacted with ATO. The latter is listed as "$Th^{\bullet+}$ consumed" in column 11. The amount of ATO consumed in reaction with $Th^{\bullet+}$ was then calculated from the sum of products containing the *tert*-octyl group. Because each molecule of ATO produces two *tert*-octyl groups, the amount of ATO consumed is given in μmol as *tert*-octyl/2 in column 12. The balance in reactants for the four runs (column 13) is seen to be reasonably close to the expected value of 0.5. Table II shows also that when MeOH was present in the initial reaction mixture (run 1), the major product was methyl ether 7, but delaying the addition of MeOH until workup (runs 2–4) led to a dominance of olefins 5 and 6.

The reaction products 10–12 of TMDAC with $Th^{\bullet+}ClO_4^-$ are given in Table III. Compounds 11 and 12 were



10 11 12

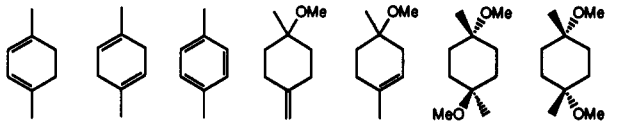
identified by comparison of GC retention times with those of authentic samples. The synthesis of 11 gave rise to an impurity in 4% yield, having a ^1H NMR signal at 4.61 ppm and a ^{13}C NMR signal at 109.2 ppm. These spectroscopic features and the method of synthesis of 11 (see Experimental Section) strongly suggested that the impurity was 10. Because one GC peak of the TMDAC/$Th^{\bullet+}ClO_4^-$ reaction mixture had exactly the same retention time as that of the assumed 10, we have assigned the structure 10 to that oxidation product. Other possible oxidation products of TMDAC are compounds 13–18, but the GC retention times of authentic 13–15 showed that these compounds were not present. Compounds 16–18 were not available



13 14 15 16 17 18

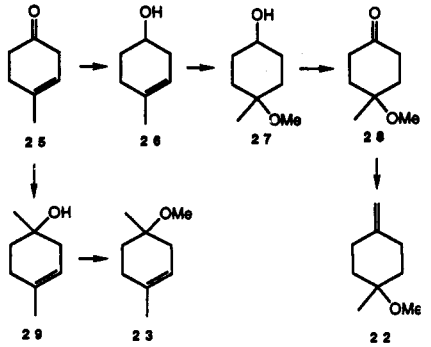
to us, but we have assumed from the relationship between structure and GC retention times of the known compounds that 16–18 were absent from our reaction mixture. Moreover, the balance of products (column 9, Table III) exceeded 95%. Reaction of TMDAC with $TBPA^{\bullet+}SbF_6^-$ (see later) was studied, and compounds 10–12 were identified but were not assayed.

As seen in Table IV, oxidation of Me_2DBO by $TBPA^{\bullet+}SbF_6^-$ gave compounds 19–24 in high total yield.



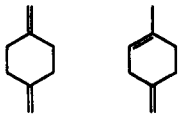
19 20 21 22 23 24t 24c

Authentic samples of these products were used for quantification by the "standard additions" method.[17] The synthesis of 22 and 23 is outlined below. Possible product 30 was shown to be absent by use of an authentic sample,



25 26 27 28 29 23 22

but no search for diene 31 was made and it could have been formed in very low yield. In view of the high (Me_2DBO + alkyl) balance (column 15), authentic samples of other conceivable products were not prepared.



30 31

Nitrogen Yields. Our principal method of judging azoalkane reactivity is to determine the yield of nitrogen at a reactant ratio (cation radical salt–azoalkane) of 1:1 and 2:1. The exacting protocol for carrying out these reactions with exclusion of air is described in the Experimental Section. In the simplest mechanistic analysis, oxidation of an azoalkane to two alkyl cations or to a dictation requires 2 equiv of cation radical salt $ArH^{\bullet+}$ and produces 1 equiv of N_2 plus 2 equiv of the neutral species ArH, eq 3. At a reactant ratio of 1:1, half of the $ArH^{\bullet+}$

$$RN{=}NR + 2ArH^{\bullet+} \rightarrow 2R^+ + N_2 + 2ArH \quad (3)$$

should oxidize azoalkane (eq 4) and the other half of the $ArH^{\bullet+}$ should preferentially oxidize the resulting radical (eq 5). With the exception of methyl, alkyl radicals have

$$RN{=}NR + ArH^{\bullet+} \rightarrow R^{\bullet} + N_2 + R^+ + ArH \quad (4)$$

$$R^{\bullet} + ArH^{\bullet+} \rightarrow R^+ + ArH \quad (5)$$

lower ionization potentials than their parent azoalkanes and are therefore likely to be oxidized more easily than the azoalkanes.[19,20] This stoichiometry (eq 3) predicts that the yields of both N_2 and recovered azoalkane should be 50% at a 1:1 reactant ratio.

Measurements of N_2 yields were carried out on reactions in two different solvents. Acetonitrile was used first, because it is a commonly used solvent in cation radical and anodic chemistry, it readily dissolves the $ArH^{\bullet+}$ salts and a variety of azoalkanes, and it does not react with $ArH^{\bullet+}$ salts. The disadvantages of acetonitrile were that it could not be dried completely and that Ritter-type products from reactions of TMDAC and Me_2DBO may have been nonvolatile diamides, not conducive to GC analysis. Therefore, the solvent mixture CH_2Cl_2/MeOH was chosen for further work. Although complete removal of water was again not possible, the trapping of cations by MeOH gave methyl ether products that were more amenable to GC analysis. The solubility of the $ArH^{\bullet+}$ salts was also somewhat greater in this solvent.

Nitrogen yields from reactions in acetonitrile are given in Table V (runs 1–27) while those from reactions in CH_2Cl_2/MeOH are in Table VI (runs 28–44). $ArH^{\bullet+}$ salts hydrolyze in wet solvents and also may lead in their reactions to proton formation. Therefore, reactions were carried out both in the absence and presence of the hindered base 2,6-di-*tert*-butylpyridine (DTBP), as indicated in column 4 under reactant ratio. For the most part, the results correspond with those anticipated from eqs 3–5; that is, at reactant ratios of 1:1 the N_2 yields cluster around 50%, while at the ratios of 2:1 the yields are mainly near 100% (e.g., runs 9–15 and 22–27 of Table V and most of the runs in Table VI). There are some notable exceptions, however. For example, in 1:1 reactions of TMDAC the N_2 yields (runs 3, 18–20, 30) are approximately 100%. Again, 1:1 reaction of ATO with $TBPA^{\bullet+}SbCl_6^-$ (run 2) led to N_2 yields that increased with greater delay between the times of mixing the reactants in MeCN and measuring the amount of N_2 (cf. run 2). When the N_2 yield exceeds that predicted by eq 3–5, we shall refer to the processes responsible for this behavior as "secondary oxidation". These anomalous results called for further studies of the effect of $ArH^{\bullet+}$ counter ions on N_2 yields.

Table V. Yields of Nitrogen from Reactions of Azoalkanes in Acetonitrile

run no.	$ArH^{\bullet+}$ salt	azoalkane	reactant ratio[a]	% N_2[b]
1	$TBPASbCl_6$	ATO	2.0:1.0	99,[c] 99, 100
2[d]	$TBPASbCl_6$	ATO	1.0:1.0	61, 72, 92
3	$TBPASbCl_6$	TMDAC	1.0:1.0:2.0	99
4	$TBPASbCl_6$	TMDAC	0.50:1.0:2.0	73[e]
5	$TBPASbCl_6$	TMDAC	0.50:1.0:2.1	92[e]
6	$TBPASbCl_6$	TMDAC	0.31:1.0:2.0	51
7	$TBPASbCl_6$	TMDAC	0.31:1.0:2.0	45
8	$TBPASbCl_6$	TMDAC	0.10:1.0:2.0	21
9	$TBPASbCl_6$	Me_2DBO	2.0:1.0:2.0	95
10	$TBPASbCl_6$	Me_2DBO	1.0:1.0:2.0	54
11	$ThClO_4$	ATO	2.7:1.0	97
12	$ThClO_4$	ATO	1.8:1.0	90
13	$ThClO_4$	ATO	1.3:1.0	61
14	$ThClO_4$	ATO	1.1:1.0	43
15	$ThClO_4$	ATO	1.0:1.0	50
16	$ThClO_4$	TMDAC	2.6:1.0	99
17	$ThClO_4$	TMDAC	2.4:1.0	99
18	$ThClO_4$	TMDAC	1.0:1.0	97
19	$ThClO_4$	TMDAC	1.0:1.0	102
20	$ThClO_4$	TMDAC	1.0:1.0:1.1	102
21	$ThClO_4$	TMDAC	1.1:1.0	97
22	$ThClO_4$	Me_2DBO	2.6:1.0	97
23	$ThClO_4$	Me_2DBO	2.3:1.0	95
24	$ThClO_4$	Me_2DBO	1.1:1.0	52
25	$ThClO_4$	Me_2DBO	0.96:1.0	54
26	$ThClO_4$	ATB	2.0:1.0	105
27	$ThClO_4$	ATB	1.0:1.0	54

[a] Initial mole ratio of $ArH^{\bullet+}$ salt to azoalkane to added base DTBP, if any. [b] Based on azoalkane. [c] 2 equiv of DTBP. [d] The three results are from runs that varied with time elapsed (1.0, 2.0, 14 h) before N_2 determination. [e] Run 5 corresponds to a greater elapsed time before N_2 determination than run 4.

Table VI. Yields of Nitrogen from Reaction of Azoalkanes in 3:1 CH_2Cl_2–MeOH

run no.	$ArH^{\bullet+}$ salt	azoalkane	reactant ratio[a]	% N_2[b]
28	$TBPASbCl_6$	ATO	1.0:1.0:2.1	53
29	$TBPASbCl_6$	ATO	2.0:1.0:2.0	99
30	$TBPASbCl_6$	TMDAC	1.0:1.0:2.0	91
31	$ThClO_4$	TMDAC	2.0:1.0:0	99[c]
32	$ThClO_4$	TMDAC	1.0:1.0:0	57
33	$ThBF_4$	TMDAC	0.97:1.0:0	44
34	$ThBF_4$	TMDAC	0.83:1.0:0	50
35	$TBPASbF_6$	ATO	1.0:1.0:2.2	50[d]
36	$TBPASbF_6$	ATO	2.0:1.0:2.0	97
37	$TBPASbF_6$	ATO	1.0:1.0:2.2	50
38	$TBPASbF_6$	TMDAC	0.51:1.0:2.1	25
39	$TBPASbF_6$	TMDAC	1.0:1.0:2.1	46
40	$TBPASbF_6$	TMDAC	2.0:1.0:2.1	96
41	$TBPASbF_6$	Me_2DBO	1.0:1.0:2.0	48
42	$TBPASbF_6$	Me_2DBO	2.0:1.0:2.0	103
43	$TBPASbF_6$	Me_2DBO	2.0:1.0:2.0	88
44	$TBPASbF_6$	Me_2DBO	2.1:1.0:2.1	89

[a] Initial mole ratio of $ArH^{\bullet+}$–azoalkane–DTBP. [b] Based on azoalkane. [c] 3:2 CH_2Cl_2–MeOH. [d] Observed 57% corrected for dissolved air.

Secondary Oxidation. The anomalously high N_2 yields in runs 3, 18–20, and 30 and the upward drift of the N_2 yield in run 2 led us to suspect that the ClO_4^- and $SbCl_6^-$ anions were somehow serving as oxidants. Supporting evidence was found in the continued decrease in the amount of unused ATO when excess ATO was reacted with $TBPA^{\bullet+}SbCl_6^-$ in both CH_3CN and 1:1 CH_2Cl_2/MeOH. That is, after the $TBPA^{\bullet+}$ had been consumed, as judged by the disappearance of its blue color, GC analysis showed that the amount of unused ATO continued to diminish with time, reaching zero in 48 h. In a similar way, the

Table VII. Yields of Nitrogen from Reactions of ATO and TMDAC with "Oxidizing Anions"

run no.	reagent 1	azoalkane	reagent 2	reactant ratio[a]	solvent	% N_2
45	$HClO_4$[b]	TMDAC		0.95:1.0	CH_2Cl_2	15
46	$HClO_4$[b]	TMDAC		0.95:1.0	CH_2Cl_2	21
47	$HClO_4$[b]	TMDAC	Th	1.0:1.0:1.0	CH_2Cl_2	99
48	$HClO_4$[b]	TMDAC		1.0:1.0	MeCN	0
49	$HClO_4$[b]	TMDAC	Th	1.0:1.0:1.0	MeCN	0
50	H_2SO_4	TMDAC		1.0:1.0	CH_2Cl_2	0
51	H_2SO_4	TMDAC		1.0:1.0	MeCN	0
52	$HClO_4$[b]	ATO	Th	1.1:1.0:1.0	CH_2Cl_2	0
53	$HClO_4$[b]	ATO		1.0:1.0	MeCN	0
54	$HClO_4$[b]	ATO		2.1:1.0	MeCN	0
55	$(n\text{-}Bu_4)NClO_4$	TMDAC		1.0:1.0	3:2 CH_2Cl_2–MeOH	0
56	$(n\text{-}Bu_4)NClO_4$	TMDAC	Th	1.0:1.0:1.0	3:2 CH_2cl_2–MeOH	0
57	$(n\text{-}Bu_4)NClO_4$	TMDAC	DTBP	1.0:1.0:1.0	3:2 CH_2Cl_2–MeOH	0
58	$(n\text{-}Bu)_4NClO_4$	TMDAC		1.0:1.0	CH_2Cl_2	0
59	Et_4NSbCl_6	TMDAC		1.0:1.0	3:1 CH_2Cl_2–MeOH	32
60	Et_4NSbCl_6	TMDAC	TBPA	1.0:1.0:1.0	3:1 CH_2Cl_2–MeOH	87
61	Et_4NSbCl_6	TMDAC	DTBP	1.0:1.0:2.2	3:1 CH_2Cl_2–MeOH	24
62	Et_4NSbCl_6	TMDAC	TBPA[c]	1.0:1.0:1.0	3:1 CH_2Cl_2–MeOH	92
63	Et_4NSbCl_6	ATO		1.0:1.0	3:1 CH_2Cl_2–MeOH	1.8
64	Et_4NSbCl_6	ATO	DTBP	1.0:1.0:2.0	3:1 CH_2Cl_2–MeOH	0
65	Et_4NSbCl_6	ATO	TBPA	1.0:1.0:1.0	3:1 CH_2Cl_2–MeOH	79
66	Et_4NSbCl_6	ATO	TBPA	1.0:1.0:1.0	3:1 CH_2Cl_2–MeOH	68
67	Et_4NSbCl_6	ATO	TBPA[d]	1.0:1.0:1.0	3:1 CH_2Cl_2–MeOH	38

[a] Initial mole ratio of reagent 1–azoalkane–reagent 2. [b] 70% $HClO_4$. [c] 1.0 equiv of DTBP added. [d] 2.0 equiv of DTBP added.

amount of TMDAC remaining after reaction with $TBPA^{\bullet+}SbCl_6^-$ in MeCN in the presence of DTBP diminished so quickly that accurate assay by GC could not be achieved. These observations implicated ClO_4^- (e.g., runs 18–21) and $SbCl_6^-$ (e.g., runs 2 and 30) as secondary oxidants. The rapid decay of TMDAC suggested that this azoalkane was more susceptible to secondary oxidation than ATO; in fact, secondary oxidation using $Th^{\bullet+}ClO_4^-$ was apparent with TMDAC (runs 18–21) but not with ATO (run 15). As a further comparison, Me_2DBO appeared not to be subject to secondary oxidation at all (e.g., runs 10 and 24). The susceptibility of TMDAC, ATO, and Me_2DBO to secondary oxidation followed their order in vertical ionization potentials (7.89, 8.00, and 8.13 eV, respectively.[19] The involvement of ClO_4^- and $SbCl_6^-$ was further emphasized by results of reactions with cation radicals paired with different counter ions, namely $Th^{\bullet+}BF_4^-$ and $TBPA^{\bullet+}SbF_6^-$. Secondary oxidation of TMDAC did not occur when $Th^{\bullet+}BF_4^-$ (runs 33, 34) and $TBPA^{\bullet+}SbF_6^-$ (runs 38, 39) were used. In the latter cases also, no further oxidation of TMDAC occurred over a period of even 9 days after mixing the reactants.

In an effort to identify the oxidizing species, a series of reactions was carried out between ATO and TMDAC and the troublesome anions but in the absence of cation radicals. The results are given in Table VII (runs 45–67) and are discussed below.

We were interested in the effect of perchloric acid on our azoalkanes[21] because the reactions of ATO and TMDAC with $Th^{\bullet+}ClO_4^-$ that produced alkenes and ethers must have formed $HClO_4$, and because $Th^{\bullet+}ClO_4^-$ is hydrolyzed by water that may be present in the solvents. Table VII shows that 70% $HClO_4$ does not decompose ATO (runs 52–54) in either MeCN or CH_2Cl_2, nor does it decompose TMDAC in MeCN (runs 48–49). Although the $HClO_4$ byproduct from $Th^{\bullet+}ClO_4^-$ oxidations surely contains less water than the 70% $HClO_4$ used here, we were loathe to deal with 100% $HClO_4$ in our control experiments. Nevertheless, 70% $HClO_4$ does cause some decomposition of TMDAC in CH_2Cl_2 (runs 45 and 46), perhaps because 70% $HClO_4$ may be a stronger acid in CH_2Cl_2 (runs 45 and 46) than in MeCN (run 48).[22] The complete decomposition of TMDAC when both $HClO_4$ and Th are present (run 47) suggests that $HClO_4$ converts Th into $Th^{\bullet+}$; in fact, $Th^{\bullet+}ClO_4^-$ is synthesized by the reaction of Th with $HClO_4$.[23] TMDAC was stable to H_2SO_4 in each solvent (runs 50 and 51). In contrast to the effect of $HClO_4$, ClO_4^- does not decompose TMDAC in CH_2Cl_2 (run 58) and is also without effect in the mixed solvents CH_2Cl_2/MeOH (runs 55–57) in which $Th^{\bullet+}ClO_4^-$ caused facile evolution of N_2 (runs 31 and 32, Table VI).

The most pronounced anion effects are seen with $SbCl_6^-$, added as $Et_4N^+SbCl_6^-$. This salt hardly oxidizes ATO (runs 63 and 64) but causes moderate (32%) decomposition of TMDAC (run 59). The effect of $SbCl_6^-$ on TMDAC is magnified by the presence of TBPA (run 60), and the same enhancement is seen with the otherwise inert ATO (runs 65 and 66). Thus, TBPA serves as an oxidation promoter, perhaps analogous to the role of a cosensitizer in electron-transfer photochemistry.[24] Since $SbCl_6^-$ is known to oxidize triphenylamine to $Ph_3N^{\bullet+}$,[25,26] the combination of $SbCl_6^-$ and TBPA may lead to $TBPA^{\bullet+}$ formation. However, in accord with the recent report by Eberson and Olofsson,[18] a solution of TBPA and Et_4NSbCl_6 in CH_2Cl_2 showed no signs of reaction either by GC or UV–vis spectroscopy, even on heating to 60 °C for 24 h. Since the presence of DTBP moderated the effect of the combination of Et_4NSbCl_6 and TBPA on ATO (run 67) we postulated that both $SbCl_6^-$ and acid were necessary for efficient reoxidation of TBPA. In another control experiment, 0.1 M $H_3O^+SbCl_6^-$[27] was reacted with 0.1 M TBPA in CH_2Cl_2

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(21) Azoalkanes can form salts in reaction with strong acids. See: Nelsen, S. F.; Blackstock, S. C.; Frigo, T. B. *J. Am. Chem. Soc.* **1984**, *106*, 3366; *Tetrahedron* **1986**, *42*, 1769. Heyman, M. L.; Snyder, J. P. *J. Am. Chem. Soc.* **1975**, *97*, 4416.

(22) $HClO_4$ and CH_3CN form a complex that slowly undergoes proton transfer. See: Kinugasa, M.; Kishi, K.; Ikeda, S. *J. Phys. Chem.* **1973**, *77*, 1914.

(23) Murata, Y.; Shine, H. J. *J. Org. Chem.* **1969**, *34*, 3368.

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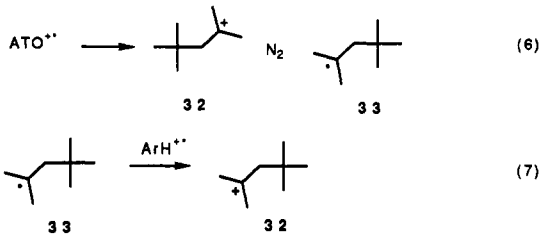
(26) See also Spange, S.; Heublein, G. *Z. Anorg. Allg. Chem.* **1989**, *571*, 181.

in a degassed, sealed tube. The solution turned intensely blue and exhibited a permanent 726-nm absorption band corresponding to a 2.5% conversion to $TBPA^{\bullet+}$. This experiment suggests a key role for the protons that arise from alkyl cations during the normal oxidation of azoalkanes by $TBPA^{\bullet+}SbCl_6^-$. In combination with adventitious water, these protons may generate $H_3O^+SbCl_6^-$, which then reoxidizes TBPA. These results explain the major features of the excess oxidizing power found for some cation radical salts listed in Tables V and VI, but we are not yet able to understand all of the details.

In our earlier work[2] on 1,1'-azoadamantane (AA), we found unexpectedly high N_2 yields using $Th^{\bullet+}ClO_4^-$ in MeCN. The 72–78% N_2 yield obtained at a 1:1 reactant ratio was attributed to escape of admantyl radicals ($Ad^\bullet$) from oxidation (eq 5), leaving more $Th^{\bullet+}$ to oxidize AA. Recent experiments on AA suggest that secondary oxidation could have been responsible for the anomalously high N_2 yields. The low solubility of AA in MeCN is another potential problem since local depletion of $Th^{\bullet+}$ near the surface of AA could have allowed $Ad^\bullet$ to escape oxidation.

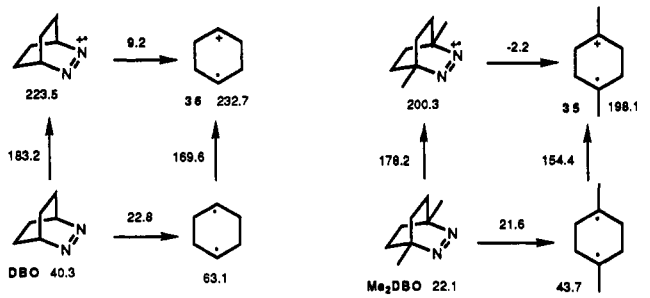
The Mechanism of Oxidative Deazatation. When secondary oxidation is absent, the stoichiometry of these reactions is in accord with eqs 3–5. That is, 1 equiv of $ArH^{\bullet+}$ leads to 50% of N_2 and 50% of recovered azoalkane, while 2 equiv of $ArH^{\bullet+}$ lead to 100% of N_2 and no remaining azoalkane. The product balances are generally 100 ± 10%, leaving little room for the occurrence of other reactions.

The simplest way of looking at these oxidations is that they are a succession of single electron transfer (SET) steps during which the azoalkane fragments. For example, after the first SET step with ATO, the $ATO^{\bullet+}$ would fragment into a *tert*-octyl cation (**32**), N_2, and a *tert*-octyl radical



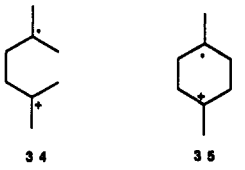
(**33**, eq 6). The latter would be oxidized immediately to **32** (eq 7). The reaction products (Table I) are then attributable to reactions of **32**; with MeOH to give **7**, with the small amount of adventitious water to give **8**, and with base to give alkenes **5** and **6**. The ratio of methyl ether to alkenes, i.e., **7**/(**5** + **6**), in Table I is 1.34, 1.50, 1.75, and 0.67 (runs 1–4), while analogous ratios in Table II are 1.60, 0.067, 0.067, and 0.083. The data show that under similar reaction conditions the ratio is reasonably independent of the nature and number of equivalents of $ArH^{\bullet+}$ (e.g., runs 1–3 of Table I and run 1 of Table II). The ratio in run 4, Table I, is significantly lower than in runs 1–3. We attribute that difference to the dominant formation of **5** in run 4, caused by base-induced elimination in *tert*-octyl chloride (**9**), a small amount of which, in fact, survived. The formation of **9** resulted from the $SbCl_6^-$ counterion.[18] The very low ratios (runs 2–4) in Table II are attributed to the fact that MeOH and base were added after the oxidation reactions were finished, by which time most of **32** had lost a proton. Supporting evidence that products **5**–**8** arise from **32** is found in the ratio of alkenes, **5**/**6**. This ratio ranges from 4.9 to 7.9 in runs 1–3 (Table I) and 1–4 (Table II) and compares favorably with the ratio 4.3 that was obtained in the solvolysis of *tert*-octyl halides.[28]

Scheme I. Gas-Phase Thermodynamic Cycle (kcal/mol) for Fragmentation of $DBO^{\bullet+}$ and $Me_2DBO^{\bullet+}$ [a]



[a] Adiabatic ionization potentials[19,20] are shown beside vertical arrows while heats of formation (ΔH_f) are given below each structure.

A common feature in the SET view of the oxidations of ATO, TMDAC, and Me_2DBO is that each initially formed azoalkane cation radical loses N_2 to give a tert-cation and tert-radical. Since TMDAC would give **34** and Me_2DBO would give **35**, the driving force for the loss of N_2 would



be similar in all three cases. In contrast, the failure of DBO to give N_2 could be attributed to the less favorable fragmentation of $DBO^{\bullet+}$ than $Me_2DBO^{\bullet+}$. SET from the bicyclic azoalkanes to $TBPA^{\bullet+}$ is endothermic because $E_{1/2}(ox)$ of TBPA is 1.06 V vs SCE[10] and the corresponding values for DBO and Me_2DBO are 1.27 and 1.19 V, respectively. The latter were estimated from the peak potentials for the irreversible oxidation of these azoalkanes in MeCN (E_{pa} = 1.12 and 1.04 V vs Ag/Ag^+, respectively) by subtracting 0.15 V from E_{pa} and then adding 0.30 V to convert from Ag/Ag^+ to SCE. Since deazatation of azoalkane cation radicals is rapid (see below), this irreversible process must drive the overall reaction of tertiary azoalkanes despite the endothermicity of the initial SET step.[29]

By means of a simple thermodynamic cycle (cf. Scheme I), we estimate that gas-phase fragmentation of $DBO^{\bullet+}$ is 11.4 kcal/mol more difficult than of $Me_2DBO^{\bullet+}$. This scheme was constructed from experimental heats of formation (ΔH_f)[30] and adiabatic ionization potentials (IP_a)[19] of the azoalkanes. ΔH_f of the biradicals was calculated by group additivity using the most recent ΔH_f of alkyl radicals[31] and assuming negligible interaction of the radical centers. Finally, IP_a of the biradicals was taken as that of the corresponding alkyl radicals;[20] that is, no special stability was attributed to the distonic ions[32] **35** and **36**.[33,34] Support for this approach is found by calculating ΔH_f of

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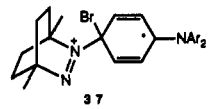
(34) Guo, Q.-X.; Qin, X.-Z.; Wang, J. T.; Williams, F. *J. Am. Chem. Soc.* **1988**, *110*, 1974.

36 as the sum of the ΔH_f (29.9 kcal/mol)[35] and IP_a (9.0 eV)[36] of bicyclo[2.2.0]hexane, whose ionization presumably also gives 36. The result, 237 kcal/mol, is not far from the ΔH_f of 36 shown in Scheme I. Gas-phase fragmentation of $Me_2DBO^{\bullet+}$ is calculated to be only slightly exothermic while $DBO^{\bullet+}$ is actually endothermic. However, deazatation of both azoalkane cation radicals, and in fact of such cation radicals in general, is much more favorable than of the neutral. Because of solvation, fragmentation is probably still more favorable in solution; consequently, electrochemical oxidation of azoalkanes is irreversible[2] and the ESR signals of most azoalkane cation radicals decay rapidly, even at rather low temperatures.[15] The oxidation potential of *tert*-butyl radical (0.09 V vs SCE)[37] is lower than predicted by Miller's correlation[38] implying a sizeable solvation energy for this ion and presumably, by analogy, for 35 and 36.

Since DBO is converted to adducts 1 and 2, an alternative mechanism for oxidative deazatation comes to mind wherein some azoalkanes add initially to $Th^{\bullet+}$ and $TBPA^{\bullet+}$. This nucleophilic attack of RN=NR on the cation radical salt may occur when oxidative fragmentation (eq 4) is energetically unfavorable.[3] For example, the nitrogens of Me_2DBO are sterically accessible and they could attack $TBPA^{\bullet+}$ to form an adduct 37 that ultimately



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fragments. In the case of DBO, the stability of the adduct would be attributable to the required formation of less stable secondary alkyl cations.

It is interesting to note that stronger oxidants (as $SbCl_6^-$ salts in MeCN) lead to a greater N_2 yield from a given azoalkane. For example, *trans*-azonorbornane (3) yields no N_2 with $TBPA^{\bullet+}$ as oxidant[39] (2:1:6 reactant ratio) but the more powerful tris(2,4-dibromophenyl)aminium analog ($TDPA^{\bullet+}$) affords 79% N_2.[16] In preliminary experiments, the same trend is seen with DBO where $TBPA^{\bullet+}$ gives no N_2 but $TDPA^{\bullet+}$ produces 47.8% N_2 (both 2:1:0 reactant ratio). The data for 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH) are $TBPA^{\bullet+}$ (1:1:7) 2.4% and $TDPA^{\bullet+}$ (1:1:2) 35.9%, while for 4-isopropylidene-3,3,5,5-tetramethyl-1-pyrazoline they are $TBPA^{\bullet+}$ (1:1:6) 0% and $TDPA^{\bullet+}$ 23% (0.9:1:0). Although these observations are of considerable practical importance, they still do not define the mechanism.

Summary. The cation radical salt induced oxidation of tertiary azoalkanes to cation-derived products has been shown to be a general reaction whether the azo group be acyclic, cyclic, or bicyclic. The hydrocarbon cations are trapped by methanol to yield methyl ethers or else they undergo elimination to olefins. Product balances are high, and the reaction stoichiometry clearly requires 2 equiv of cation radical salt to one of azoalkane. Although the details of the mechanism are not yet certain, and indeed may vary from case to case, fragmentation of an azoalkane cation radical or nucleophilic attack of the azo linkage on the cation radical salt are the most likely possibilities. Secondary oxidation complicates the study of some azoalkane–cation radical salt reactions when the counterion is $SbCl_6^-$ or ClO_4^- but not SbF_6^- or BF_4^-. Neither protons alone nor ClO_4^- itself cause secondary oxidation but inclusion of the neutral Th or TBPA in the reaction mixture greatly enhances the nitrogen yield. On the basis of many control experiments, it appears that this complication arises in part from reoxidation of Th or TBPA by $HClO_4$, $H_3O^+SbCl_6^-$, or perhaps even by $SbCl_6^-$.

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(39) Addition of 5 mol % of $TBPA^{\bullet+}SbCl_6^-$ to *cis*-azo-1-norbornane in the presence of 30 mol % DTBP caused rapid, quantitative conversion to the trans isomer. In view of recent published results,[16] this catalytic reaction no doubt proceeds via the azoalkane cation radical.

Table VIII. Description of GC Columns Used

name[a]	packing/coating	source	dim.
	packed columns		L(ft) × i.d.(in.)
A	10% FFAP ChW 60–80 DMCS AW	lab	20 × 0.25
B	5Å Mol Sieves. 60–80	lab/HP	4 × 0.125
	open tubular columns	FT[b] (μm)		L(m) × o.d.(mm)
C	SE-54	0.25	HP	25 × 0.25
D	SE-54	1.20	Alltech	15 × 0.54
E	DB-FFAP	0.31	J&W	15 × 0.31
F	SE-30	2.65	HP	12 × 0.53
G	DB-1	0.25	J&W	30 × 0.25

[a] Designation used in text. [b] Film thickness.

Experimental Section

General. Melting and boiling points are uncorrected except as noted; melting points were obtained with a Mel-Temp apparatus. CH_2Cl_2 and MeCN used for gas-yield determinations were freshly distilled from CaH_2 under N_2 or were refluxed over P_2O_5 under Ar for 12 h and then distilled and stored under Ar. MeOH was either freshly distilled from CaH_2 under N_2 or was refluxed over Mg activated with I_2 under Ar and then distilled and stored under Ar. Solvents dried for use in synthesis were distilled from CaH_2, except THF and Et_2O, which were freshly distilled from benzophenone ketyl radical. HPLC, TLC, and column chromatography eluents were Omnisolv or Baker spectrophotometric grade.

NMR spectra were obtained on a JEOL FX-90Q, an IBM AF-300, or an IBM AF-250 spectrometer using $CDCl_3$ solvent unless specified otherwise. Chemical shifts (δ, ppm) are reported using internal TMS or solvent signal ($CDCl_3$, ^1H δ = 7.25, ^{13}C δ = 77.0; CD_3CN, ^1H δ = 1.95, ^{13}C δ = 117.7 or 1.30) as reference. UV–vis spectra were run on either a Cary 17 or a Hewlett-Packard 8452A diode array spectrophotometer. Low-resolution mass spectra were obtained on a Finnigan 3300 spectrometer and high-resolution mass spectra (HRMS) on a CEC Du Point 21-110B spectrometer.

GC analyses were conducted on either a Hewlett-Packard 5890 gas chromatograph interfaced to an IBM XT compatible computer or on a Varian 3700 GC attached to a Spectra Physics 4270 computer–intergrator. The "standard addition" method[17] used for quantitative analysis requires that one first determine the peak area ratio of product to internal standard. A known weight of the authentic product is added and the ratio is redetermined. The weight of product present initially is then calculated from the two ratios. The GC columns employed are referred to by the designation given in Table VIII.

Compounds. The syntheses of Me_2DBO,[40] TMDAC,[41] and ATO[42] have been reported elsewhere. TBPA, DTBP, and DBMP are commerically available and were purified by distillation or sublimation. Thianthrene (Fluka) was purified by column chromatography on silica gel using ligroin as eluent and crystallized from acetone, mp 156–157.5 °C. $Th^{\bullet+}ClO_4^-$[23] and $Th^{\bullet+}BF_4^-$[43] were synthesized as described earlier. The perchlorate is explosive,

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as noted in the original procedure.

Tris(4-bromophenyl)aminium hexachloroantimonate ($TBPA^{\bullet+}SbCl_6^-$) was prepared by reacting TBPA with $SbCl_5$.[44] The crude material was recrystallized until its melting point (dec) exceeded 141 °C.

Tris(4-bromophenyl)aminium hexafluoroantimonate ($TBPA^{\bullet+}SbF_6^-$) was prepared similarly to $TBPA^{\bullet+}ClO_4^-$.[44] Under N_2, 1.25 g (2.58 mmol) TBPA and 0.887 g (2.58 mmol) $AgSbF_6$ were stirred in 20 mL of dry Et_2O. The mixture was immersed in a CCl_4/CO_2(s) slush bath (−23 °C), and 0.52 g (2.05 mmol) of I_2 in 13 mL of dry Et_2O was added dropwise. The solution turned deep blue immediately. After 30 min, the cold bath was removed and the reaction was stirred overnight. The reaction solution was filtered under N_2 through a frit of medium porosity, and the solids were washed with 15 mL Et_2O until no I_2 color was observed in the washings. The collection vessel beneath the frit was changed, and the remaining solids were washed successively with 5-mL portions of dry CH_2Cl_2 until the blue cation radical salt had been removed from the Ag salts. The blue CH_2Cl_2 solution was then poured into an 8-fold excess of dry Et_2O to precipitate $TBPA^{\bullet+}SbF_6^-$. The blue crystals were isolated by vacuum filtration, washed with 2 × 10 mL of Et_2O, and dried in a vacuum desiccator to yield $TBPA^{\bullet+}SbF_6^-$ (1.26 g; 1.76 mmol) in 68% yield. Iodometric titration with standardized $Na_2S_2O_3$ of I_2 produced from the reaction of the radical cation with KI in dry MeCN typically showed the purity to be greater than 97%. Recrystallization from CH_2Cl_2/Et_2O increased the purity but markedly reduced the yield.

Tetraethylammonium hexachloroantimonate ($Et_4N^+SbCl_6^-$) was prepared by the literature procedure[25] and recrystallized twice from $MeCN/CCl_4$, mp 277–9 °C dec (lit.[25] mp 276 °C dec).

2-Methoxy-2,4,4-trimethylpentane (7) was prepared by solvomercuration–demercuration[45] of commericially available diisobutylene with $Hg(OAc)_2$ in MeOH as in the synthesis of **27** (see below): bp 80–1 °C (99 mmHg); ^{1}H NMR (90 MHz) δ 3.17 (s, 3 H), 1.48 (s, 2 H), 1.20 (s, 6 H), 1.00 (s, 9 H); ^{13}C NMR (23 MHz) δ 76.10, 51.49, 48.86, 31.52, 31.25, 27.18.

2,4,4-Trimethyl-1-pentene (5) was isolated by spinning-band distillation of commercial diisobutylene: bp 94.1 °C; ^{1}H NMR (90 MHz) δ 4.82 (m, 1 H), 4.63 (br s, 1 H), 1.95 (s, 2 H), 1.76 (m, 3 H), 0.91 (s, 9 H).

2,4,4-Trimethylpentan-2-ol (8) was synthesized by oxymercuration–demercuration of diisobutylene with $Hg(OAc)_2$ in H_2O[46] or by reaction of MeMgCl with 4,4-dimethyl-2-pentanone. This alcohol had bp 42–45 °C (10 mmHg) (lit.[47] bp 42–47 °C (7 mmHg)): ^{1}H NMR (90 MHz, CD_3CN) δ 2.22 (br s, 1 H), 1.48 (s, 2 H), 1.22 (s, 6 H), 1.02 (s, 9 H).

2-Chloro-2,4,4-trimethylpentane (*tert*-Octyl Chloride) (9). A 1.25-mL (16.8-mmol) portion of $SOCl_2$ was cautiously added to 1.46 g (11.2 mmol) of **8** with stirring at 0 °C. A vigorous reaction occurred immediately, and the mixture was stirred for 10 min at 0 °C. A 1.25-mL portion of $SOCl_2$ was then added, and the mixture was refluxed for 30 min at 80 °C. *tert*-Octyl chloride (1.16 g; 7.80 mmol) was isolated by vacuum distillation in 70% yield, bp 77–9 °C (81 mmHg): ^{1}H NMR (90 MHz) δ 1.88 (s, 2 H), 1.69 (s, 6 H), 1.05 (s, 9 H).

2-Methoxy-2,5-dimethylhex-4-ene (11) was prepared by methylation of 2,5-dimethylhex-4-en-2-ol[48] with NaH/MeI as in the synthesis of **22** (see below). Isolation of **11** (110 mg; t_R = 21.0 min) as a clear oil was achieved by preparative GC, column A, inj. 181 °C; det. 173 °C; col. 100 °C; flow rate 26 mL/min: ^{1}H NMR (300 MHz) δ 5.15–5.05 (br m, 1 H), 3.13 (s, 3 H), 2.08 (d, 2 H; J = 7.2 Hz), 1.64 (s, 3 H), 1.53 (s, 3 H), 1.05 (s, 6 H); ^{13}C NMR (75 MHz) δ 133.23, 120.04, 75.30, 49.15, 38.10, 25.93, 24.94, 17.86.

2,5-Dimethoxy-2,5-dimethylhexane (12) was prepared similarly to **11** by methylation of commerically available 2,5-dimethylhexane-2,5-diol with NaH/MeI: bp 98–9 °C (37 mmHg); ^{1}H NMR (90 MHz) δ 3.18 (s, 3 H), 1.49 (s, 4 H), 1.15 (s, 6 H) (lit.[49] ^{1}H NMR δ 3.10 (s, 3 H), 1.40 (s, 4 H), 1.10 (s, 6 H)); ^{13}C NMR (23 MHz, $CDCl_3$) δ 74.50, 49.19, 33.53, 25.18.

4-Methylcyclohex-3-en-1-one (25) was prepared by acid hydrolysis of 4-methoxy-1-methylcyclohexa-1,4-diene obtained as the Birch reduction product from commercially available 4-methylanisole: bp 74 °C (19 mmHg) (lit.[50] bp 70–3 °C (20 mmHg)); ^{1}H NMR (90 MHz) δ 5.40 (br m, 1 H), 2.80 (m, 2 H), 2.15–2.50 (m, 4 H), 1.75 (br s, 3 H) (lit.[51] ^{1}H NMR δ 5.44 (br m, 1 H), 2.83 (m, 2 H), 2.45 (m, 4 H), 1.78 (m, 3 H)). GC analysis revealed that **25** (t_R = 3.72 min) was contaminated with 15% 4-methylcyclohexanone (t_R = 3.51 min) and less than 1% 4-methylanisole (t_R = 4.07 min); column C, inj. 200 °C; det. 250 °C; oven temp. prog.: 100 °C for 3 min, ramp 5 °C/min. 4-Methylcyclohexanone was identified by GC/MS on column D using similar conditions. **25** was used without further purification.

4-Methylcyclohex-3-en-1-ol (26). To a stirred solution of 1.40 g (37.0 mmol) of $NaBH_4$ in 50 mL of absolute EtOH at 0 °C was added dropwide 4.09 g (37.1 mmol) **25**. After 45 min, the ice bath was removed, and stirring was continued for 135 min. A 15-mL portion of H_2O was added, and the mixture was neutralized by dropwise addition of 15% H_2SO_4. The mixture was extracted with 3 × 25 mL of Et_2O, the organic phases were combined and dried over $MgSO_4$, and the Et_2O was removed on a rotary evaporator. Vacuum distillation afforded 2.42 g (21.6 mmol) of crude **26**, bp 100–2 °C (39 mmHg) (lit.[52] bp 61–2 °C (5 mmHg)), 58% yield. NMR analysis of the two components isolated by preparative GC revealed that the product was composed of 80% **26** (t_R = 9.9 min) and 20% 4-methylcyclohexanol (t_R = 7.5 min); column A, inj. 180 °C; det. 180 °C; col. 180 °C; flow rate 28 mL/min. 4-Methylcyclohexanol was identified by ^{1}H NMR but was not removed prior to using **26** to make **27**: ^{1}H NMR (300 MHz) δ 5.26 (br s, 1 H), 3.92 (m, 1 H), 2.31 (br d, 1 H; J = 16.5 Hz), 2.02–1.57 (m, 4 H), 1.64 (br s, 3 H), 1.50 (d, 1 H; J = 4.5 Hz). ^{13}C NMR (75 MHz) δ 134.03, 118.14, 66.97, 34.48, 31.12, 28.22, 23.39.

1,4-Dimethylcyclohex-3-en-1-ol (29).[53] A 1.20-mL (18-mmol) portion of MeI was added dropwise to 0.525 g (21.6 mmol) of Mg turnings in 10 mL of Et_2O under N_2. Rapid boiling was observed upon addition of a small I_2 crystal. After the exotherm subsided, the solution was refluxed for 30 min and then cooled in an ice bath. A 1.90-g (17.2-mmol) portion of **25** was added dropwise, and the solution was refluxed for 30 min. After cooling to room temperature, the solution was carefully poured onto 50 mL of crushed ice. The aqueous layer was acidified with aqueous NH_4Cl, saturated with NaCl, and extracted with 2 × 20 mL of Et_2O. The organic phases were combined, dried over $MgSO_4$, and concentrated in a rotary evaporator. Vacuum distillation afforded 0.711 g (5.63 mmol) of product, bp 100 °C (51 mmHg), 31% yield. GC/MS analysis revealed that the product was composed of 88% **29** (t_R = 3.8 min) and 12% 1,4-dimethylcyclohexanol (t_R = 3.1 min) having M^+ 126 and 128, respectively; column D, inj. 150 °C; oven temp. prog.: 70 °C for 2 min, ramp 6 °C/min. NMR analysis of **29** (t_R = 27.0 min) was carried out on the oil isolated by preparative GC; column A, inj. 180 °C; det. 180 °C; col. 140 °C; flow rate 30 mL/min: ^{1}H NMR (250 MHz) δ 5.28 (br s, 1 H), 2.25–1.85 (m, 4 H), 1.67 (s, 2 H), 1.58 (s, 3 H), 1.24 (s, 3 H); ^{13}C NMR (75 MHz) δ 133.54, 118.79, 68.47, 39.85, 35.45, 28.47, 27.89, 23.35.

1-Methoxy-1,4-dimethylcyclohex-3-ene (23) was prepared by methylation of **29**.[54] Under N_2, the mineral oil was removed from 0.965 g (20.1 mmol) of 50% NaH in mineral oil by three successive washings with 5 mL of dry hexane. A 14-mL portion of dry THF and 1.25 mL (20.1 mmol) of MeI were added, and

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the slurry was warmed to 50–5 °C. A 1.69-g (13.4-mmol) portion of **29** was added dropwise. After 2.5 h, the solution was cooled to room temperature and added to 20 mL of saturated NH_4Cl at 0 °C. Et_2O (15 mL) was added, the phases were separated, and the aqueous phase was extracted with 3 × 25 mL of Et_2O. The organic phases were combined and dried over $MgSO_4$, and the solvent was rotary evaporated. GC analysis, using the same conditions as for **25**, revealed that the product was composed of 88% **23** (t_R = 8.59 min) and 12% *cis*- and *trans*-4-methoxy-1,4-dimethylcyclohexane (t_R = 7.37 and 8.18 min). Isolation of **23** (82 mg; t_R = 21.6 min) as a colorless oil was achieved by preparative GC; column A, inj. 175 °C; det. 196 °C; col. 72 °C; flow rate 27 mL/min: ^1H NMR (300 MHz) δ 5.26 (br s, 1 H), 3.27 (s, 3 H), 1.67 (br s, 3 H), 2.20–1.50 (br m, 6 H), 1.16 (s, 3 H); ^{13}C NMR (75 MHz) δ 133.20, 116.51, 72.55, 48.84, 36.61, 31.97, 28.09, 23.23, 22.55. Anal. Calcd for $C_9H_{16}O$ (M^+): 140.1201. Found: 140.1202. Anal. Calcd for $(M + 1)^+$: 141.1235. Found: 141.1236.

4-Methoxy-4-methylcyclohexan-1-ol (27). A 4.00-g (35.6-mmol) portion of **26** was added dropwise to 11.4 g (35.6 mmol) of $Hg(OAc)_2$ in 50 mL of dry MeOH. After stirring for 15 min, the solution was cooled with an ice bath and 36 mL of 3 M NaOH was added dropwise. After 5 min, 36 mL of 0.5 M $NaBH_4$ in 3 M NaOH was added dropwise. Stirring was continued until a majority of the Hg had settled, such that the solution could be decanted. After neutralization by careful addition of 15% HCl, this solution was vacuum filtered through a Celite pad and the pad was rinsed with Et_2O. The phases were separated, and the aqueous phase was washed with 2 × 30 mL of Et_2O. The organic phases were combined and dried over $MgSO_4$, and the Et_2O was removed with a rotary evaporator. GC analysis revealed that 90.7% of the product was **27**. The ratio of **27t** (trans MeO, OH) (t_R = 11.09 min) to **27c** (t_R = 11.44 min) was 29:1). The remainder of the product consisted of 6.6% 4-methylcyclohexanol (t_R = 5.47 min) and 2.6% **26** (t_R = 4.42 min); column E, inj. 180 °C; det. 250 °C; oven temp. prog.: 70 °C for 2 min, ramp 5 °C/min to 100 °C, ramp 10 °C/min. Vacuum distillation afforded 2.26 g (15.7 mmol) of 95% pure **27**, bp 133–5 °C (52 mmHg), 44% yield. **27** was used without further purification. Structural confirmation was completed on the oil isolated by preparative GC; column A, inj. 170 °C; det. 170 °C; col. 150 °C; flow rate 25 mL/min. Since **27t** and **27c** were not completely resolved under these conditions, three fractions of the two peaks were collected. The NMR spectra of fraction one showed only **27t**. The NMR data reported here for **27c** were taken as the difference between fractions one and three. Significant overlap of the ring methylene resonances prevented complete assignment of the ^1H NMR of **27c**. Although the correct assignment of the lower boiling component with the shorter GC t_R to **27t** and the higher boiling component with the longer GC t_R to **27c** is not required for the product study, we mention our reasoning for completeness. The much higher *A* value[55] of CH_3 relative to MeO and OH suggests that CH_3 will occupy the equatorial position in both isomers. In that case, OH will be axial in **27t** and equatorial in **27c**. The chemical shift of the axial H α to OH is 3.38 ppm while that of equatorial H α to OH is 3.89 ppm.[56] These values are in good accord with our structural assignment of **27t** and **27c**: ^1H NMR (250 MHz) **27t** δ 3.90 (br s, 1 H), 3.17 (s, 3 H), 2.06–1.43 (m, 9 H), 1.15 (s, 3 H); **27c** δ 3.56 (br s, 1 H), 3.16 (s, 3 H), 1.09 (s, 3 H); ^{13}C NMR (63 MHz) **27t** δ 73.29, 67.43, 48.83, 31.18, 29.77, 23.33; **27c** δ 71.95, 70.29, 48.53, 33.79, 30.82, 24.05.

4-Methoxy-4-methylcyclohexan-1-one (28) was prepared by the addition of 9 mL of Jones Reagent to 1.51 g (10.5 mmol) of **27** in 10 mL of acetone at 0 °C. After 1 h of stirring at 0 °C and 0.5 h stirring at room temperature, the reaction was complete, as shown by TLC with 10% EtOAc in hexane on silica gel (**28**, R_f = 0.17; **27**, R_f = 0.04). A pinch of $NaHSO_3$ was added to consume the excess Jones Reagent. Brine (10 mL) was added, and the phases were separated. The aqueous phase was washed with 2 × 20 mL of Et_2O. The organic phases were combined and dried over $MgSO_4$, and the solvent was rotary evaporated. The product **28** (0.694 g; 4.88 mmol) was isolated in 46% yield. GC analysis, using the same conditions as for **27**, showed that the product was composed of 77.5% **28** (t_R = 8.95 min), 16.4% 4-methylcyclohexanone (t_R = 3.47 min), and 5.2% **25** (t_R = 5.42 min). GC/MS analysis revealed that **28** (t_R = 20.5 min) and **26** (t_R = 13.0 min) exhibited molecular ions at m/e = 142 and 112, respectively, using similar conditions with column F. Characterization of **28** (t_R = 18.6 min) was completed on the colorless oil isolated by preparative GC; column A, inj. 182 °C; det. 188 °C; col. 170 °C; flow rate 25 mL/min: ^1H NMR (250 MHz) δ 3.26 (s, 3 H), 2.56 (d of t, 2 H; J = 6.3 and 14 Hz), 2.12 (m, 4 H), 1.66 (d of t, 2 H; J = 4.9 and 14 Hz), 1.21 (s, 3 H) (lit.[57] ^1H NMR (CCl_4) δ 3.13 (s, 3 H), 1.56–2.56 (m, 8 H), 1.20 (s, 3 H)). ^{13}C NMR (63 MHz) δ 212.11, 71.98, 49.20, 36.91, 35.48, 23.41.

4-Methoxy-4-methyl-1-methylenecyclohexane (22).[58] Into a 50-mL three-neck Morton flask equipped with two pressure-equalizing addition funnels was placed 1.30 g (5.25 mmol) of $CeCl_3$. The solid was heated at 140 °C at less than 1 Torr for 1 h with stirring. After being cooled to room temperature, the apparatus was brought to 1 atm with N_2. A 15-mL portion of dry THF was added via syringe. The slurry was stirred for 2 h, and the flask was cooled to −78 °C with a dry ice/*i*-PrOH bath. Via cannula, one funnel was charged with 4.50 mL of 1 M Me_3SiCH_2Li in pentane and the other funnel with 0.427 g (3.00 mmol) of **28** in 3 mL of dry THF. With vigorous stirring, the Me_3SiCH_2Li solution was added dropwise. After 30 min, the solution of **28** was added dropwise. After being stirred for 5 h, 0.78 mL of dry TMEDA was added dropwise. The cold bath was removed 15 min later, and the solution was allowed to warm to room temperature. The solution was cautiously added to a stirred mixture of 40 mL of saturated $NaHCO_3$ and 40 mL of CH_2Cl_2. The phases were separated, and the aqueous phase was washed with 3 × 40 mL of CH_2Cl_2. The organic phases were combined and washed with 50 mL of saturated NaCl. The organic phase was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. TLC with EtOAc on silica gel demonstrated that **28** had been consumed (**28** R_f = 0.76; product R_f = 0.05). GC/MS analysis, using the same conditions as for **28**, revealed the product had four components: 5% (t_R = 13.9 min) (M^+ − OH) 182, < 1% (t_R = 14.6 min) (M^+ − OH) 182, 80% (t_R = 23.5 min) (M^+ − OH) 212, and 80% (t_R = 23.5 min) (M^+ − OH) 212. The first two components were *cis*- and *trans*-4-methyl-1-[(trimethylsilyl)methyl]cyclohexan-1-ol, and the second two components were *cis*- and *trans*-4-methoxy-4-methyl-1-[(trimethylsilyl)methyl]cyclohexan-1-ol. Without further treatment, the crude product was dissolved in 6 mL of MeCN, and 12 drops of 48% HF was added. After 1.5 h, TLC showed that the spot at R_f = 0.05 was gone and that a new spot at R_f = 0.68 was present. A 10-mL portion of H_2O was added, and the solution was neutralized with saturated $NaHCO_3$. The solution was washed with 3 × 15 mL of pentane. The organic phases were combined and dried with $MgSO_4$, and the solvent was removed with a rotary evaporator. Compound **22** (t_R = 8.7 min; 92.9%) and 4-methyl-1-methylenecyclohexane (t_R = 3.9 min; 7.1%; identified by NMR) were isolated by preparative GC; column A, inj. 175 °C; det. 196 °C; col. 72 °C; flow rate 23 mL/min: ^1H NMR (300 MHz) δ 4.63 (s, 2 H), 3.22 (s, 3 H), 2.28 (t of d, 2 H), 2.05 (d of t, 2 H), 1.76–1.90 (m, 2 H), 1.35 (t of d, 2 H), 1.14 (s, 3 H); ^{13}C NMR (75 MHz) δ 148.85, 106.77, 72.83, 48.57, 36.91, 30.42, 23.73. Anal. Calcd for $C_9H_{16}O$ (M^+): 140.1201. Found: 140.1202. Anal. Calcd for $(M + 1)^+$: 141.1235. Found: 141.1236.

1,4-Dimethoxy-1,4-dimethylcyclohexane (24t and 24c).[45] To a slurry of 5.90 g (18.5 mmol) of $Hg(OAc)_2$ in 20 mL of dry MeOH was added dropwise a solution of 2.00 g (18.5 mmol) of 1,4-dimethylenecyclohexane[59] in 10 mL of dry MeOH. After 12 min of stirring, the mixture became homogeneous. The mixture was cooled to 0 °C, and 25 mL of 3 M NaOH was added dropwise. After 2 min, a solution of 0.350 g (9.25 mmol) $NaBH_4$ in 25 mL of 3 M NaOH was added dropwise. The ice bath was removed and the mixture stirred until it reached room temperature. Hg was removed by filtration through a Celite pad. The phases were separated, and the aqueous phase was washed with 2 × 15 mL

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of pentane. The organic phases were combined, dried with $MgSO_4$, and treated with Norit, and the pentane was removed by simple distillation. Vacuum distillation of the concentrate afforded 0.70 g (4.1 mmol) of a mixture of **24t** and **24c**, bp 124–5 °C (85 mmHg), 22% yield. Isolation of **24c** (92 mg) and **24t** (122 mg) was achieved by preparative GC; column A, inj. 193 °C; det. 178 °C; col. 150 °C; flow rate 30 mL/min. HRMS analysis gave identical results on both **24t** and **24c**: ^{1}H NMR (300 MHz) **24c** δ 3.12 (s, 6 H), 1.14 (s, 6 H), 1.82–1.73 (m, 4 H; axial), 1.32–1.40 (m, 4 H; equatorial); **24t** δ 3.16 (s, 6 H), 1.11 (s, 6 H), 1.48–1.59 (m, 4 H); ^{13}C NMR (75 MHz) **24c** δ 73.12, 48.43, 32.25, 22.22; **24t** δ 72.34, 48.62, 30.81, 24.44. Anal. Calcd for $C_{10}H_{20}O_2$ (M^+): 172.1463. Found: 172.1465. Anal. Calcd for $(M + 1)^+$: 173.1497. Found: 173.1493.

Gas Yield Determination. The reaction vessels used for determining the gas evolved from a reaction had two compartments for keeping the reactants separate during degassing, two male ground glass joints for connection to the vacuum line and the Töpler pump, a constriction for sealing the vessel before the reaction was run and one for reopening it afterwards. Liquid samples (e.g., TMDAC, ATO) were added to the vessel by first introducing the liquid via syringe into an open-ended, tared capillary tube, measuring the mass, and delivering the capillary tube into the proper compartment through a small funnel. Solid samples were added via a small funnel also. DTBP or DBMP and azoalkane were added to one compartment, and the cation radical salt was added to the other compartment. The arm(s) for addition of reactants were then sealed while the tube was purged slowly with N_2. When MeOH was added as a trap, it was delivered to the azoalkane compartment via syringe. The actual reactant concentration can be calculated from the data given in Tables I–IV. The gas yield determinations (Tables V–VII) were done on 0.02–0.03 M solutions of azoalkane. Errors in transferring the samples and in measuring N_2 lead to an estimated uncertainty of ±3% in the nitrogen yield.

Freshly distilled dry CH_2Cl_2 or MeCN was syringed into an oven-dried gas bulb containing activated 4-Å molecular sieves which was then attached to the vacuum line. The solvent was freeze/thaw degassed three cycles and was then distilled into an evacuated graduated cylinder. The reactants were then degassed via three freeze/thaw cycles, and the desired solvent volume was distilled into the reaction vessel, which was then sealed at the upper constriction and allowed to warm to room temperature prior to mixing. When the reaction was judged complete based on a color change or time requirement, the lower constriction was carefully scratched with a tungsten carbide tool and the vessel was attached to the Töpler pump apparatus for N_2 measurement. The evolved N_2 was analyzed by GC on column B to ensure the absence of O_2. The solution was then subjected to GC analysis using column C for ATO and TMDAC (inj. 200 °C, det. 250 °C, oven program: 50 °C for 3 min, ramp 8 °C/min to 105 °C, ramp 10 °C/min to 170 °C). For Me_2DBO, column E was employed (inj. 100 °C, det. 250 °C, oven program: 90 °C for 2 min, ramp 5 °C/min to 110 °C).

Reactions of ATO and TMDAC with $Th^{\bullet+}ClO_4^-$ (cf. Tables II and III) were carried out as follows. A solution of azoalkane in 3:2 CH_2Cl_2–MeOH (3 mL of CH_2Cl_2 and 2 mL of dry MeOH) was prepared immediately before use in a 5-mL volumetric flask and kept under Ar. The concentration was adjusted so that 1.0 mL of solution contained the amounts of ATO and MeOH shown in Tables II and III. $Th^{\bullet+}ClO_4^-$ was weighed in a round-bottomed flask equipped with a magnetic stir bar. The flask was capped with a rubber septum and flushed with Ar. Dry CH_2Cl_2 (5 mL) was added to give a deep purple solution, and then 1.0 mL (measured in a graduated syringe) of ATO/MeOH or TMDAC/MeOH solution was added rapidly in one portion. The deep purple color of $Th^{\bullet+}$ was discharged immediately. *tert*-Butylamine (100 μL, 952 μmol) or triethylamine (100 μL, 717 μmol) was added (by syringe) to neutralize $HClO_4$ produced in using $ThClO_4$ with ATO and TMDAC, respectively. *tert*-Butylamine was chosen because it did not interface with the capillary GC analyses. The resulting yellow solution was passed through about 250 mg of 60–200 mesh silica gel contained in a disposable pipet, and the filtrate was collected in a 25-mL volumetric flask. After the solution was diluted to volume with CH_2Cl_2, two 10-mL aliquots were removed and placed in 10-mL volumetric flasks. These 10-mL aliquots were analyzed by capillary GC twice before, and twice after, the introduction of precise amounts (25–50 μmol) of authentic products. Thus, there were two analyses of each aliquot, or four analyses of the reaction as a whole. In each experiment, one analysis was rejected so that the results are the average of three GC analyses. In the case of ATO, toluene (5 μL, 47.0 μmol) was used as the internal standard for early-eluting components and benzophenone (10 mg, 54.9 μmol) was used as the standard for late-eluting components. For TMDAC, *n*-nonane (1 μL, 5.6 μmol) was used as the internal standard for early-eluting components and *n*-tetradecane (5 μL, 19.2 μmol) was used as the standard for late-eluting components. Column G in a Varian 3700 Chromatograph was used for GC analyses with an oven program: 35 °C for 10 min, ramp 15 °C/min to 270 °C, hold for 7 min.

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